



α -Telluration of 2,4,6-trimethylacetophenone under mild conditions: Role of steric factor in the solid state structures of Te(II and IV) compounds

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ABSTRACT

Elemental tellurium inserts into the C_{sp^3} -Br bond of α -bromomesitylmethyl ketone and due to its strong carbophilic character affords the crystalline C-tellurated derivative of 2,4,6-trimethylacetophenone, $(MesCOCH_2)_2TeBr_2$, **1b** in over 80% yield. Electrophilic substitution of the parent ketone with aryltellurium trichlorides, at room temperature, gives nearly quantitative yields of unsymmetrical alkylaryl-tellurium dichlorides $(MesCOCH_2)ArTeCl_2$ (Ar = mesityl, Mes, **2a**; 1-naphthyl, Np, **3a**; anisyl, Ans, **4a**). Fairly stable mesitylmethyltellurium(II) derivatives, $(MesCOCH_2)_2Te$, **1** and $(MesCOCH_2)ArTe$ (Ar = Mes, **2**; Np, **3** and Ans, **4**) obtained as the reduction products of their dihalotellurium(IV) analogues, readily undergo oxidative addition of dihalogens to afford the corresponding $(MesCOCH_2)_2TeX_2$ (X = Cl, **1a**; Br **1b**; I, **1c**) and $(MesCOCH_2)ArTeX_2$ (X = Cl, Br, I, Ar = Mes, **2a**, **2b**, **2c**; Np, **3a**, **3b**, **3c** and Ans, **4a**, **4b**, **4c**). Crystallographic structural characterization of **1**, **1b**, **2**, **2a**, **2b**, **2c**, **3**, **3a** and **4c** illustrates that the steric demand of mesityl group appreciably influences primary geometry around the 5-coordinate Te(IV) atom when it is bound directly to it. It also makes the Te atom inaccessible for the ubiquitous $Te \cdots X$ intermolecular secondary bonding interactions that result in supramolecular structures. In the crystal lattice of symmetrical telluroether **1**, an interesting supramolecular synthon based upon reciprocatory weak $C-H \cdots O$ H-bonding interaction gives rise to chains via self-assembly.

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1. Introduction

Frankland's original method for making compounds with a zinc-carbon bond [1] has since been used for other metals and metalloids including tellurium. Thus, simple dialkyltellurium diiodide results when Te is heated with an iodoalkane (or bromoalkane in the presence of NaI) [2]. The oxidative insertion of elemental Te into the C_{sp^3} -Br bond of α -bromo-substituted acylmethanes recently achieved by us provides a one-pot synthesis of keto-functionalized dialkyltellurium dibromides [3]. Another route to tellurated ketones involves electrophilic substitution of methyl ketones with $ArTeCl_3/TeCl_4$ to afford diorganotellurium dichlorides [4]. Biphasic bisulfite reduction of these diorganotellurium(IV) dihalides results in the labile Te(II) derivatives, $(RCOCH_2)_2Te$ and $(RCOCH_2)ArTe$ (Ar = 1-Np, Mes; R = Ph, Me, Et, *i*-Pr, *t*-Bu). Oxidative addition of dihalogens to these tellurides gives their dihaloTe(IV) derivatives as crystalline solids which have been characterized by spectral and diffraction studies [4]. Solid state structural characterization of

telluroethers is reported either for diaryls with C_{sp^2} -Te- C_{sp^2} or alkylaryls with C_{sp^2} -Te- C_{sp^3} groupings. Single-crystal structural studies on dialkyltellurium(II) with C_{sp^3} -Te- C_{sp^3} groupings, being liquids or low melting solids, are rare and limited to the cyclic tellurium(II) derivatives [5] and $(4-MeC_6H_4COCH_2)_2Te$ [6]. In recent years, 2,4,6-trimethylacetophenone, due to steric bulk and mesityl group-induced crystallizability, has attracted considerable attention [7] as a methyl ketone precursor to metal enolates, which themselves are useful in many organic transformations. Taking advantages of steric effect of the mesityl group and inductive (+I) effect of the ring methyl substituents in 2,4,6-trimethylacetophenone and its α -bromo derivative, stable crystalline mesitylmethyltellurium(II and IV) derivatives have been isolated in the crystalline state and structurally characterized in solution and solid state.

2. Results and discussion

2.1. Synthesis

The reaction between freshly ground tellurium powder and α -bromo-2,4,6-trimethylacetophenone, initiated at the melting point

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of the latter, is sustainable at ambient temperature in the absence of a solvent and gives the colourless bromide $(\text{MesCOCH}_2)_2\text{TeBr}_2$ (**1b**) in over 80% yield. This is interesting as the yields in the insertion reactions of elemental tellurium into $\text{C}_{\text{sp}^3}\text{-Br}$ bond of the other α -bromoacylmethanes including freshly prepared α -bromo pinacolone [3,8] are generally between 40 and 65%. Near quantitative yield of the reaction may be attributed to both the electronic and steric factors; the latter probably helps in preventing side reactions. Fig. 1 depicts a possible mechanism for the formation of symmetrical diorganotellurium dibromides from elemental Te and RCOCH_2Br . Since the intermediate alkyltellurenyl(II) halides are known to be kinetically unstable the ultimate product is formed either via route (a) or (b) [9]. However, we prefer route (a) due to the fact that MesTeBr (prepared in situ) adds $\text{MesCOCH}_2\text{Br}$ to give $(\text{MesCOCH}_2)_2\text{MesTeBr}_2$ in good yields at ambient temperature (vide infra). The first step of the mechanism may be compared with the formation of the well-known Reformatsky intermediates. Unlike the zinc reagents [10], rearrangement of the intermediate, $\text{RCOCH}_2\text{TeBr}$, to its enolate form $[\text{CH}_2=\text{C}(\text{R})\text{OTeBr}]$ does not take place (vide infra) possibly due to strong carbophilic character of tellurium.

Elemental tellurium failed to insert into the $\text{C}_{\text{sp}^3}\text{-X}$ bond of *i*-PrCOCH₂Br and MesCOCH₂Cl, even in the presence of NaI. While the former failure is surprising, the latter case may be attributed to stronger $\text{C}_{\text{sp}^3}\text{-Cl}$ bond. However, the chloro analogue of **1b**, $(\text{MesCOCH}_2)_2\text{TeCl}_2$ (**1a**) could be prepared by electrophilic substitution of the parent ketone with TeCl_4 (Scheme 1). Metathetical reactions of **1a** or **1b** with KI at room temperature afforded $(\text{MesCOCH}_2)_2\text{TeI}_2$ (**1c**) in very good yield (85% with respect to **1b**). Reduction of **1b** with a stoichiometric amount of sodium metabisulfite followed by quick separation from the aqueous layer affords the symmetrical telluroether $(\text{MesCOCH}_2)_2\text{Te}$ (**1**) as a yellow crystalline solid. It is one of the few examples of crystalline dialkyltellurides that has been characterized crystallographically. Oxidation of **1** with SO_2Cl_2 or I_2 gives the corresponding dihalide **1a** or **1c**, respectively.

Te(II), in the form of aryltellurium bromides (prepared in situ from equimolar amounts of Ar_2Te_2 and Br_2), also inserts into the $\text{C}_{\text{sp}^3}\text{-Br}$ bond of MesCOCH₂Br to afford the mixed alkylaryltellurium(IV) dibromides, $(\text{MesCOCH}_2)_2\text{ArTeBr}_2$ (Ar = Mes, **2b**; Np, **3b**). Reduction of these bromides with $\text{Na}_2\text{S}_2\text{O}_5$ affords the mixed alkylaryltelluroethers, $(\text{MesCOCH}_2)_2\text{ArTe}$ (**2** and **3**), as crystalline solids that are fairly stable at room temperature to symmetrization into $(\text{MesCOCH}_2)_2\text{Te}$ and Ar_2Te . However, the appearance of an additional signal at 340 ppm due to Np_2Te_2 in the ^{125}Te NMR spectrum of **3** indicates its slow disproportionation in CDCl_3 solution. The dichloromethane solutions of the unsymmetrical telluroethers, **2–4**, are also readily oxidized by halogen or a halogen source to form $(\text{MesCOCH}_2)_2\text{ArTeX}_2$ (Ar = Mes, X = Cl, **2a**; Br, **2b**; I, **2c**; Ar = Np; X = Cl, **3a**; Br, **3b**; I, **3c** and Ar = Anisyl; X = Cl, **4a**; Br, **4b**; I, **4c**). Mixed alkylaryltellurium(IV) dichlorides, $(\text{MesCOCH}_2)_2\text{ArTeCl}_2$ (**2a–4a**), are also obtained in quantitative yields by electrophilic substitution of the parent ketone, MesCOCH₃ with ArTeCl_3 . Unlike Reformatsky reagents, Te(IV) dibromides, **1b–3b** did not react with ketones and were recovered unchanged.

2.2. Spectroscopic studies

All the synthesized crystalline mesitylmethyltellurium(II and IV) derivatives are fairly soluble in dichloromethane and

chloroform. The $\nu(\text{CO})$ among the Te(IV) compounds appears at $1686 \pm 4 \text{ cm}^{-1}$ and at $1675 \pm 5 \text{ cm}^{-1}$ for the tellurides **1** and **2** which is lower than that in the parent ketone (1703 cm^{-1}) or its α -bromo derivative (1693 cm^{-1}). The ^1H NMR spectra show two signals in the ratio of 2:1 for *o*-Me and *p*-Me protons in the mesityl group of the acylmethyl ligand. However, the *o*-Me protons of the mesityl ligand in mesityltellurium(IV) dichloride, **2a**, appear separately due to restricted rotation about the Te–C bond. The ^1H NMR spectra of the dibromo and diiodo analogues, **2b** and **2c**, consist of more than one signal for methylene protons and multiplets for methyl protons probably due to species formed by partial decomposition in solution. Appearance of a singlet for the methylene protons for dihalides **1a–1c** even at low temperature indicates that the steric bulk of the mesityl group of the ligands does not affect the magnetic equivalence of methylene protons. A singlet for the methylene protons also appears for the mixed alkylaryltellurium dihalides, $(\text{MesCOCH}_2)_2\text{ArTeX}_2$ (except in the spectra of **2b** and **2c**). As expected these protons are shielded in case of Te(II) compounds **1** (δ 3.9), **2** (δ 4.0) and **3** (δ 4.1). The ^{13}C NMR spectra of the Te(IV) derivatives show a singlet for the carbonyl carbon at $\sim \delta$ 201, which is shifted a little to $\sim \delta$ 205 in the case of Te(II) derivatives. The methylene carbon is quite shielded in case of tellurides **1–3** compared to the Te(IV) derivatives. The ^{125}Te NMR spectra of all the products, except **2b** (where two signals appear at δ 671 and 716 in 1:1 ratio), show a single peak, indicating the presence of only one Te-containing species. The ^{125}Te chemical shift for **1b** (δ 625) is shifted upfield compared to analogous pinacolyl derivative $(t\text{-BuCOCH}_2)_2\text{TeBr}_2$ (δ 672), indicating a greater +I effect of a mesityl group compared to a *t*-Bu group (Te–C bond distances in both the compounds are the same). The signals for the Te(II) compounds are shielded as expected. A more pronounced shielding in **2** compared to **1** is indicative of the stronger +I effect of the mesityl ligand in it.

2.3. Crystal structures

The molecular structures of Te(IV) compounds **1b**, **2a–2c**, **3a**, **4c** and Te(II) compounds **1–3** were unambiguously determined by X-ray diffraction techniques. Asymmetric units in each case consist of one molecule, except in **2** where four independent molecules are present. Crystal data and structure refinement details are given in Table 1. ORTEP views of the molecular structures of **1b**, **2b**, **3a**, **4c** and **1**, showing 30% probability displacement ellipsoids, omitting H atoms for clarity, and captioned with the geometrical parameters relevant to the primary geometry, are depicted in Figs. 2–5 and 7. ORTEP views for **2a**, **2c**, **2** and **3** (Figs. S1–S4) are part of the supplementary material.

All compounds bear C-tellurated 2,4,6-trimethylacetophenone and may be described as mesitylmethyltellurium derivatives. Taking into account the equatorial lone pair at the hypervalent tellurium atom, the spatial arrangement around the central atom is best described as ψ -trigonal bipyramidal with the expected ligand atom occupancies. However, the carbonyl O atom(s) of the acylmethyl ligand(s) invariably approaches significantly closer to the Te(IV) atom compared to $\Sigma r_{\text{vdw}}(\text{Te}, \text{O})$ value of 3.58 Å. It lies almost in the equatorial C–Te–C plane, *trans* to a Te–C bond ($\angle \text{O}\cdots\text{Te}-\text{C}$ ranges from $144.686(163)^\circ$ in **1b** to $163.554(143)^\circ$ in **2b**) and thus imparts a coordination number of 5 (6 in case of **1b**) to the Te(IV) atom. The sum of endocyclic angles of the four-membered ring

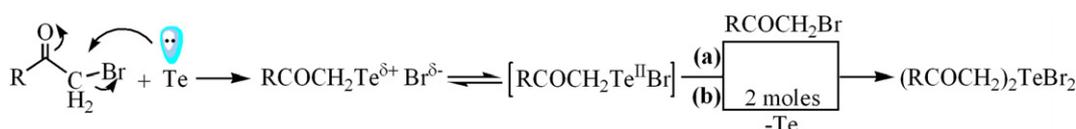
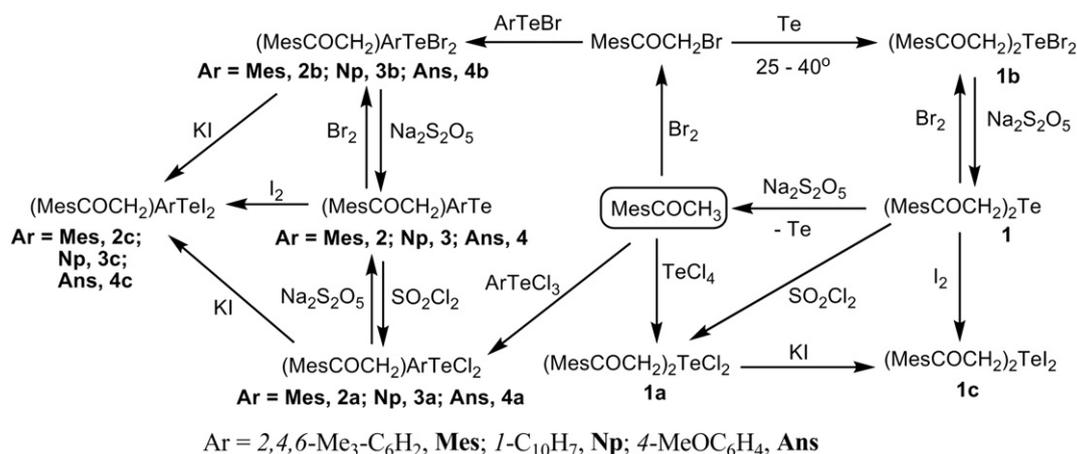


Fig. 1. Probable Mechanism of Te Insertion.



Scheme 1.

formed by the intramolecular Te···O secondary bonding interaction, being close to 360° (359.8 and 359.9° in **1b**, 359.9° in **2a**, 359.8° in **2b**, 359.9° in **2c**, 359.7° in **3a**, and 359.9° in **4c**), substantiates coplanarity of the atoms comprising it. Compound **1b**, with a six-coordinate Te atom similar to the analogous bis(acylmethyl)tellurium(IV) dihalides, (RCOCH₂)₂TeX₂ (R = Ph, 4-MeC₆H₄, *t*-Bu; X = Br, I) [3,8], conforms to a butterfly shape with perfect C_{2v} point group symmetry. But, among mesityltellurium(IV) dihalides, (MesCOCH₂)MesTeX₂, the sterically cumbersome mesityl ligand widens the equatorial C–Te–C angle appreciably (108.58(7)° in **2a**, 109.55(15)° in **2b**, and 107.41(10)° in **2c**) in comparison to the values observed for **1a–1c** or the average value of 96(3)° found for ⟨C–Te–C in the CSD for diorganotellurium dihalides [11]. The increasing deviation from linearity obvious from the X–Te–X angle is consistent with the decrease of *d*(Te–X) (X = I, 174.031(10)°; Br, 170.13(2)°; Cl, 168.712(16)°) and further substantiates the influence of steric demand of the aryl ligand on the primary geometry of Te(IV) in these compounds. Such steric congestion causes restricted rotation of the mesityl ligand about the Te–C bond, resulting in magnetic inequivalence of its *ortho* methyl and *meta* protons (vide supra) and also restricts self-assembly via intermolecular Te···X secondary bonding interactions, a characteristic feature of the lattices of organotellurium(IV) halides. As such, in the lattice of **2b**, reciprocity Te···Br secondary bonding interactions lead to dimerization only and in collaboration with C–H···OH-bonding interactions give rise to centrosymmetric pairs of molecules with planar Te₂Br₂ units (Fig. S5).

X-ray crystal structures of very few dialkyltellurium(II) compounds are known. Besides our recent report on the crystal structure of bis(4-methylbenzoyl)tellurium(II), the other dialkyltellurium derivatives for which single-crystal X-ray diffraction data are available in the literature include phenoxatellurine [5h] and substituted pentane-2,4-dionato-C1,C5-tellurium(II) chelates (Fig. 6), all of which are cyclic telluroethers.

Though acylmethyltellurium(II) derivatives are reported to be unstable to detelluration [12], yellow crystals of compound **1** are fairly stable at ambient atmospheric conditions. In the absence of axial halo ligands and enhanced electron density at the Te atom in compound **1** (when compared with the Te(IV) analogue **1b**), the organic ligands adopt a transoidal orientation about the C–Te–C plane away from the lone pair region and impart C₂ molecular symmetry.

Interestingly, the observed ⟨C–Te–C values for the Te(II) compounds in the present study, that lie in the range 95.5–99.6° (except 87.0° for one of the four independent molecules) and can

be justified by VSEPR, are quite large in comparison to those reported for the telluroethers with C_{sp3}–Te–C_{sp3} linkage (Fig. 6). Interatomic distances between Te and the O atoms in the molecular structure of **1** (3.5861(24) and 3.6027(26) Å) and **3** (3.8221(32) Å) are comparable to the Σ*r*_{vdw}(Te,O) value and the acute O···Te–C angles indicate absence of intramolecular Te···O secondary bonding interactions. While electronic and steric repulsions are responsible for the observed molecular configuration of **1**, the intermolecular Te···O (3.1175(27) Å) interaction is preferred to the intramolecular interaction and gives rise to a one-dimensional supramolecular array of molecules in the lattice of **3** (Fig. S6). However, the *d*(Te, O) and the measures of ⟨O···Te–C (trans), in the molecular structures of each of the four independent molecules present in the crystal lattice of **2** are 3.15 ± 0.05 Å and 140.50 ± 0.89°, respectively. These values fulfill the criteria of *d*(Te, O) < Σ*r*_{vdw}(Te, O) and near linearity of the O···Te–C (trans) triad, for the presence of intramolecular 1,4-Te···O secondary bonding interactions. The occurrence of intramolecular in preference to intermolecular Te···O secondary bonding interactions in case of **2** may be due to difference in the steric influence of the aryl ligands. Orientation of the aryl ring bound to Te in **2** and **3** is nearly orthogonal to the C–Te–C plane, with the interplanar angle between the C–Te–C plane and average plane of the ring atoms lying in the range of 67.1–83.5°. It may be said that 1,4-Te···O secondary bonding interactions are too subtle to influence the molecular geometry of α-tellurated acylmethanes and that it is determined primarily by the electronic and steric effects of the ligands bonded to the tellurium atom.

The parametric details of the observed intermolecular C–H···O and C–H···X (X = Cl, Br, I) interactions are listed in Table S1. In the crystal lattice of **1**, an elegant supramolecular synthon based upon C–H···O hydrogen bonding is realized, where each acylmethyl fragment, consisting of (methylene)C–H as H-bond donor and carbonyl O as H-bond acceptor, behaves as a *plug and socket* pair to extend a chain on either side of each molecule (Fig. S7). One-dimensional arrays of molecules in the lattice of **1b** (Fig. S8) are the result of (methylene)C–H···Br interactions.

3. Experimental

3.1. General considerations

Preparative work was performed under dry nitrogen. Melting points were recorded in capillary tubes and are uncorrected. α-Bromo-2,4,6-trimethylacetophenone was prepared as per the

Table 1
Summary of crystallographic and data processing parameters for (MesCOCH₂)₂Te, **1**; (MesCOCH₂)NpTe, **2**; (MesCOCH₂)MesTe, **3**; (MesCOCH₂)₂TeBr₂, **1b**; (MesCOCH₂)NpTeCl₂, **2a**; (MesCOCH₂)MesTeCl₂, **3a**; (MesCOCH₂)MesTeBr₂, **3b**; (MesCOCH₂)MesTeI₂, **3c**; (MesCOCH₂)AnsTeI₂, **4c**.

	1	2	3	1b	2a	2b	2c	3a	4c
Formula	C ₂₂ H ₂₆ O ₂ Te	C ₂₀ H ₂₄ O ₂ Te	C ₂₁ H ₂₀ O ₂ Te	C ₂₂ H ₂₆ Br ₂ O ₂ Te	C ₂₀ H ₂₄ Cl ₂ O ₂ Te	C ₂₀ H ₂₄ Br ₂ O ₂ Te	C ₂₀ H ₂₄ I ₂ O ₂ Te	C ₂₁ H ₂₀ Cl ₂ O ₂ Te	C ₁₈ H ₂₀ I ₂ O ₂ Te
Formula weight	450.03	407.99	415.97	609.85	478.89	567.79	661.79	486.87	649.74
Temperature (K)	200(2)	200(2)	200(2)	200(2)	200(2)	200(2)	200(2)	296(2)	200(2)
Wavelength, λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Triclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	<i>Pca</i> 2 ₁	<i>P</i> 12 ₁ 1	<i>P</i> 12 ₁ / <i>c</i> 1	<i>Pna</i> 2 ₁	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1	<i>Pna</i> 2 ₁	<i>Pbca</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	7.8870(2)	8.7755(4)	23.0867(13)	11.8618(9)	16.8488(4)	9.6692(5)	7.3119(2)	10.8740(3)	24.3111(6)
<i>b</i> (Å)	15.3130(6)	29.892(2)	7.9797(5)	31.146(3)	8.3543(2)	9.6841(5)	13.1120(4)	17.4945(5)	9.20800(10)
<i>c</i> (Å)	16.4850(6)	13.8304(9)	9.5954(4)	6.2930(7)	14.4008(4)	12.3034(5)	23.1457(5)	21.5467(5)	9.4402(2)
α	90	90	90	90	90	108.972(4)	90	90	90
β	90	91.659(6)	100.377(5)	90	99.990(2)	105.160(4)	90	90	96.275(2)
γ	90	90	90	90	90	96.121(4)	90	90	90
<i>V</i> (Å ³)	1990.95(12)	3626.5(4)	1738.80(16)	2324.9(4)	1996.32(9)	1028.12(9)	2219.06(10)	4098.94(19)	2100.59(7)
<i>Z</i>	4	8	4	4	4	2	4	8	4
δ _{calc} (mg/m ³)	1.501	1.495	1.589	1.742	1.593	1.834	1.981	1.578	2.055
μ _{calc} (mm ⁻¹)	1.506	1.641	1.713	4.730	1.762	5.337	4.127	1.718	4.362
Completeness to θ max (%)	99.2	99.2	99.4	99.0	99.3	99.2	99.4	98.7	99.1
<i>F</i> (000)	904	1632	824	1184	952	548	1240	1920	1208
Size (mm ³)	0.55 × 0.45 × 0.22	0.55 × 0.35 × 0.12	0.46 × 0.36 × 0.17	0.44 × 0.37 × 0.28	0.44 × 0.35 × 0.30	0.47 × 0.35 × 0.21	0.55 × 0.42 × 0.15	0.57 × 0.41 × 0.29	0.49 × 0.44 × 0.15
<i>h</i> , <i>k</i> , <i>l</i> ranges collected	-11 → 11 -22 → 12 -24 → 23	-13 → 13 -45 → 34 -20 → 20	-30 → 34 -12 → 10 -14 → 14	-17 → 17 -47 → 43 -8 → 9	-25 → 22 -12 → 10 -21 → 20	-14 → 14 -14 → 14 -17 → 18	-10 → 11 -19 → 19 -31 → 33	-16 → 14 -26 → 25 -29 → 30	-35 → 36 -13 → 13 -14 → 14
θ range (°)	4.70–32.44	4.65–32.49	4.53–32.53	4.75–32.62	4.76–32.50	4.55–32.47	4.67–32.57	4.69–32.53	4.74–32.58
Reflection collected	11 754	36 925	16 072	30 385	18 061	15 728	35 393	24 299	33 455
Data/restraints/parameters	5877/1/232	19 310/511/722	5767/0/211	7485/1/250	6601/0/224	6758/0/224	7418/1/223	6848/0/230	7140/0/215
<i>R</i> (<i>F</i>) ^a	0.0357	0.1082	0.0456	0.0537	0.0243	0.0388	0.0232	0.0305	0.0371
<i>R</i> _w (<i>F</i> ²) ^b	0.0894	0.3217	0.0940	0.0721	0.0580	0.1088	0.0413	0.0587	0.0843
GoF(<i>F</i> ²)	0.946	1.175	0.963	0.843	1.068	1.107	0.942	0.904	1.053
Largest diff. peak/hole (eÅ ⁻³)	1.858/–0.339	5.137/–2.930	1.684/–0.817	1.069/–1.117	0.796/–0.735	1.702/–1.676	0.581/–0.602	1.102/–0.738	1.660/–1.220

$$^a R = \sum ||F_c| - |F_o|| / \sum |F_o|$$

$$^b R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$$

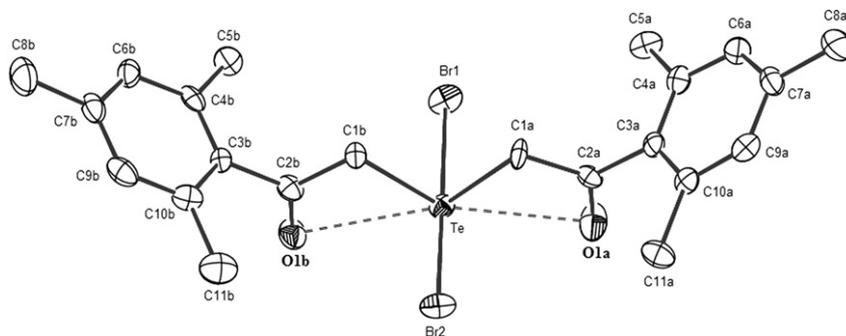


Fig. 2. Molecular structure of **1b**. Selected interatomic distances (Å) and angles (°): Te–C1a = 2.113(2), Te–C1b = 2.135(2), Te–Br1 = 2.6691(13), Te–Br2 = 2.6617(13), Te···O1 = 2.936(6), Te···O2 = 2.949(3); C1a–Te–C1b = 93.4(3), Br1–Te–Br2 = 172.37(3), O1a···Te–C1b = 145.8(2), O1b···Te–C1a = 144.7(2).

literature method [13]. 1-Naphthyl, mesityl and anisyltellurium trichlorides were prepared by the chlorination of the corresponding ditelluride. IR spectra were recorded as KBr pellets using a Perkin–Elmer RX1 spectrometer. The electrospray mass spectra were recorded on a Micromass Quattro II triple quadrupole spectrometer setting ESI capillary at 3.5 kV and the cone voltage at 40 V. The data are averaged over six to eight scans. ^1H NMR spectra were recorded at 300.13 MHz in CDCl_3 on a Varian DRX 300 spectrometer using Me_4Si as internal standard solution. $^{13}\text{C}\{^1\text{H}\}$ (100.54 MHz) and $^{125}\text{Te}\{^1\text{H}\}$ (126.19 MHz) NMR spectra were recorded in CDCl_3 on a JEOL Eclipse Plus 400 NMR spectrometer, using Me_4Si and Me_2Te , respectively, as internal standards. UV spectra were recorded on a Shimadzu UV-1700 spectrophotometer. Microanalyses were carried out using a Carlo Erba 1108 analyzer. Tellurium was estimated volumetrically.

3.2. Insertion of elemental Te into $\text{C}_{\text{sp}3}$ –Br bond of α -bromo-2,4,6-trimethylacetophenone

Compound 1b: Freshly ground tellurium powder (0.64 g, 5.0 mmol) and α -bromo-2,4,6-trimethylacetophenone (1.62 g, 10.0 mmol) were stirred together at $\sim 40^\circ\text{C}$ for 24 h. The resulting solid was extracted with CH_2Cl_2 (20 mL) and precipitated with hexane to give crude **1b**, which was recrystallized from CH_2Cl_2 as colourless needle shaped crystals. Yield: 2.95 g (84%). M.p.: 205°C . $\nu(\text{CO})$: 1686 cm^{-1} . Anal. Calcd. for $\text{C}_{22}\text{H}_{26}\text{O}_2\text{Br}_2\text{Te}$: C, 43.33; H, 4.30; Te, 20.92. Found: C, 43.52; H, 4.25; Te, 21.10. ^1H NMR: $\delta = 2.30$ (s, 3H, *p*-Me), 2.31 (s, 6H, *o*-Me), 5.15 (s, 2H, CH_2), 6.88 (s, 2H, aryl) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 19.41$ (*p*-Me), 21.14 (*o*-Me), 60.68 (CH_2), 128.99, 133.80, 133.98, 140.27 (C-aryl), 208.48 (CO) ppm. $^{125}\text{Te}\{^1\text{H}\}$ NMR: $\delta = 625$ ppm. ES-MS m/z : 469.1 $[\text{M} - 2\text{Br} + \text{OH}]^+$, 531.0

$[\text{M} - \text{Br}]^+$, 612.0 $[\text{M}]^+$, 627.0 $[\text{M} + \text{OH}]^+$, 1239.1 $[2\text{M} + \text{OH}]$. λ_{max} in CHCl_3/nm ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$): 252 (38 560), 242 (15 950).

3.3. Electrophilic substitution reactions of 2,4,6-trimethylacetophenone with ArTeCl_3

Compound 2a: Mesityltellurium trichloride (0.35 g, 1.0 mmol) and 2,4,6-trimethylacetophenone (0.32 g, 2.0 mmol) were stirred together at room temperature under a flow of dry nitrogen (~ 12 h). The resulting solid was dissolved in diethyl ether and addition of ethanol afforded colourless solid $(\text{MesCOCH}_2)\text{MesTeCl}_2$ (**2a**) which was recrystallized as rectangular crystals from CH_2Cl_2 . Yield: 0.32 g (66%). M.p.: 177°C . Anal. Calcd. for $\text{C}_{20}\text{H}_{24}\text{OCl}_2\text{Te}$: C, 50.16; H, 5.05; Te, 26.64. Found: C, 49.80; H, 5.18; Te, 27.58. $\nu(\text{CO})$: 1690 cm^{-1} . ^1H NMR: $\delta = 2.32$ (s, 6H, *p*-Me), 2.34 (s, 6H, *o*-Me), 2.65 (s, 3H, *o*-Me), 2.83 (s, 3H, *o*-Me), 5.38 (s, 2H, CH_2), 6.91 (s, 2H, aryl), 6.98 (s, 1H, aryl), 7.01 (s, 1H, aryl) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 19.30$, 21.00, 21.15, 23.62, (*o*-Me and *p*-Me), 24.19 (CH_2), 128.94, 130.35, 131.46, 133.82, 134.27, 134.68, 140.02, 140.28, 141.09, 142.32 (C-aryl), 201.67 (CO) ppm. $^{125}\text{Te}\{^1\text{H}\}$ NMR: $\delta = 755$ ppm. ES-MS m/z : 425.1 $[\text{M} - 2\text{Cl} + \text{OH}]^+$, 445.1 $[\text{M} - \text{Cl}]^+$, 499.0 $[\text{M} + \text{OH}]^+$, 571.2 $[\text{M} - 2\text{Cl} + \text{MesCOCH}_2]^+$.

Compound 3a: A mixture of 1-naphthyltellurium trichloride (0.36 g, 1.0 mmol) and 2,4,6-trimethylacetophenone (0.32 g, 2.0 mmol) was stirred slowly at room temperature under a flow of dry nitrogen (~ 12 h). The resulting paste was washed with cold petroleum ether (3×10 mL), triturated with diethyl ether and filtered to remove excess 2,4,6-trimethylacetophenone. The residue was dissolved in chloroform and filtered through a short silica column. Concentration of the extract to about one third and addition of diethyl ether afforded colourless solid $(\text{MesCOCH}_2)\text{NpTeCl}_2$

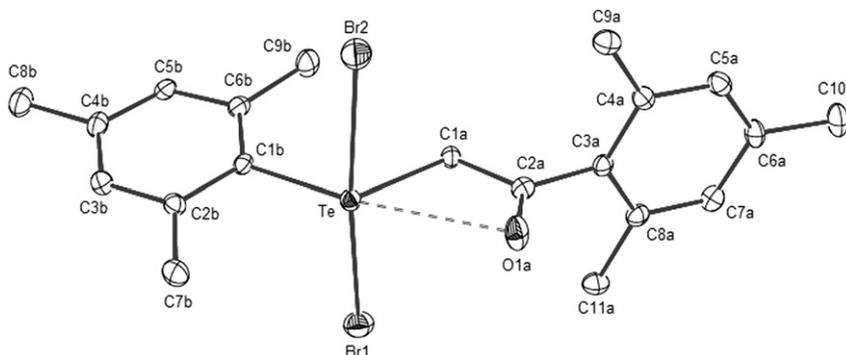


Fig. 3. Molecular structure of **2b**. Selected interatomic distances (Å) and angles (°): Te–C1a = 2.151(4), Te–C1b = 2.133(5), Te–Br1 = 2.6447(7), Te–Br2 = 2.6636(7), Te···O = 2.829(4); C1a–Te–C1b = 109.5(2), Br1–Te–Br2 = 170.13(2), O1a···Te–C1b = 163.6(1).

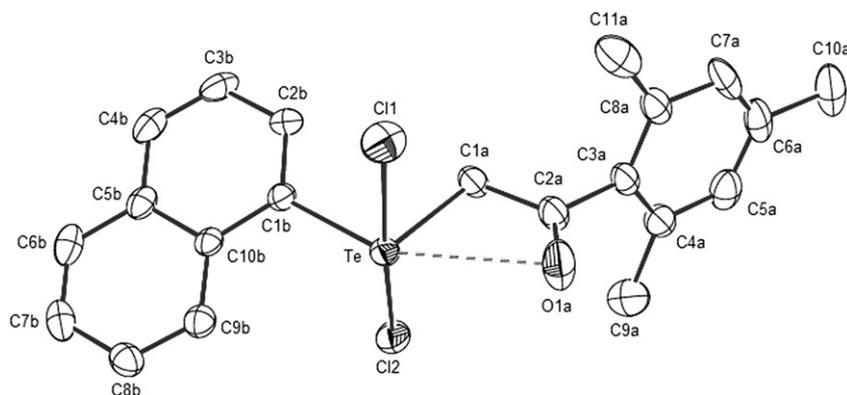


Fig. 4. Molecular structure of **3a**. Selected interatomic distances (Å) and angles ($^{\circ}$): Te–C1a = 2.121(3), Te–C1b = 2.126(3), Te–Cl1 = 2.5146(9), Te–Cl2 = 2.485(1), Te \cdots O = 2.880(3); C1a–Te–C1b = 98.8(1), Cl1–Te–Cl2 = 171.72(3), O1a \cdots Te–C1b = 151.9(1).

(**3a**). Yield: 0.41 g (85%). M.p.: 185 $^{\circ}$ C. Anal. Calcd. for $C_{21}H_{20}OCl_2Te$: C, 51.80; H, 4.14; Te, 26.21. Found: C, 51.50; H, 4.10; Te, 27.00. $\nu(CO)$: 1687 cm^{-1} . 1H NMR: δ = 2.32 (s, 3H, *p*-Me), 2.37 (s, 6H, *o*-Me), 5.60 (s, 2H, CH_2), 6.92 (s, 2H, aryl), 7.56–8.17 (m, 7H, aryl) ppm. $^{13}C\{^1H\}$ NMR: δ = 19.32 (*p*-Me), 21.17 (*o*-Me), 71.12 (CH_2), 126.37, 126.81, 127.34, 128.29, 128.99, 129.46, 131.95, 132.57, 132.76, 132.88, 132.81, 134.13, 134.31, 140.33 (C-aryl), 201.47 (CO) ppm. $^{125}Te\{^1H\}$ NMR: δ = 741 ppm.

Compound 4a: A solution of anisyltellurium trichloride (0.34 g, 1.00 mmol) and 2',4',6'-trimethylacetophenone (0.32 g, 2.0 mmol) in dry chloroform (10 mL) was heated to reflux for 3 h, cooled and filtered through a short silica column. Concentration of the resulting solution and addition of petroleum ether afforded colourless crystalline solid (MesCOCH₂)AnsTeCl₂ (**4a**). Yield: 0.54 g (68%). M.p.: 190 $^{\circ}$ C. Anal. Calcd. for $C_{18}H_{20}O_2Cl_2Te$: C, 46.31; H, 4.32; Te, 27.33. Found: C, 46.80; H, 4.20; Te, 27.50. $\nu(CO)$: 1686 cm^{-1} . 1H NMR: δ = 2.29 (s, 3H, *p*-Me), 2.32 (s, 6H, *o*-Me), 3.86 (s, 3H, OMe), 5.11 (s, 2H, CH_2), 6.88 (s, 2H, aryl), 7.03 (d, 2H, aryl), 8.09 (d, 2H, aryl) ppm. $^{13}C\{^1H\}$ NMR: δ = 19.29 (*p*-Me), 21.13 (*o*-Me), 55.55 (OMe), 71.73 (CH_2), 115.73, 117.46, 128.93, 133.77, 134.13, 135.67, 140.15, 162.33 (C-aryl), 201.41 (CO) ppm. $^{125}Te\{^1H\}$ NMR: δ = 823 ppm.

3.4. Reduction of **1b**, **2a**, **3a** and **4a** to **1**, **2**, **3** and **4**

Compound 1: Reduction of **1b** (0.31 g, 0.50 mmol) in dichloromethane (50 ml) with an aqueous solution of $Na_2S_2O_5$ (0.09 g,

0.5 mmol) was carried out for 30 min. As soon as the organic layer turned yellow it was quickly separated, washed with water (4×50 mL) and dried over anhydrous Na_2SO_4 . Concentration of the filtrate to about one third and addition of diethyl ether afforded a yellow solid that was dissolved in CH_2Cl_2 /hexane (3:1) and cooled to ~ 10 $^{\circ}$ C for 24 h to give yellow needle shaped crystals of the telluride **1**. Yield: 0.12 g (51%). M.p.: 72–74 $^{\circ}$ C. Anal. Calcd. for $C_{22}H_{26}O_2Te$: C, 58.71; H, 5.82; Te, 28.35. Found: C, 59.02; H, 5.94; Te, 28.10. $\nu(CO)$: 1671 cm^{-1} . 1H NMR: δ = 2.22 (s, 3H, *p*-Me), 2.56 (s, 6H, *o*-Me), 3.91 (s, 2H, CH_2), 6.85 (s, 2H, aryl) ppm. $^{13}C\{^1H\}$ NMR: δ = 16.12 (*p*-Me), 20.04 (*o*-Me), 21.06 (CH_2), 128.72, 134.18, 137.39, 139.14 (C-aryl), 205.11 (CO) ppm. $^{125}Te\{^1H\}$ NMR: δ = 386 ppm.

Compound 2: A solution of **2a** (0.48 g, 1.00 mmol) in dichloromethane (~ 50 mL) was shaken with an aqueous solution of $Na_2S_2O_5$ (0.19 g, 1.0 mmol) for 1 h. The organic layer gradually turned yellow. It was separated, washed (4×50 mL) with water and dried over anhydrous Na_2SO_4 . Volatiles were removed under reduced pressure. The resulting yellow oil was dissolved in hexane (5 ml) and cooled in a freezer overnight to give yellow rectangular crystals of the telluride **2**. Yield: 0.24 g (58%). M.p.: 61 $^{\circ}$ C. Anal. Calcd. for $C_{20}H_{24}OTe$: C, 58.88; H, 5.93; Te, 31.27. Found: C, 58.80; H, 5.50; Te, 30.90. $\nu(CO)$: 1678 cm^{-1} . 1H NMR: δ = 2.26 (s, 6H, *p*-Me), 2.27 (s, 6H, *o*-Me), 2.53 (s, 6H, *o*-Me), 4.01 (s, 2H, CH_2), 6.81 (s, 2H, aryl), 6.92 (s, 2H, aryl). $^{13}C\{^1H\}$ NMR: δ = 19.52, 20.11, 20.89, 21.02 (*o*-Me, *p*-Me), 29.50 (CH_2), 117.04, 127.29, 128.58, 133.83, 137.82, 138.81, 139.40, 145.39 (C-aryl), 205.85 (CO) ppm. $^{125}Te\{^1H\}$ NMR: δ = 296 ppm.

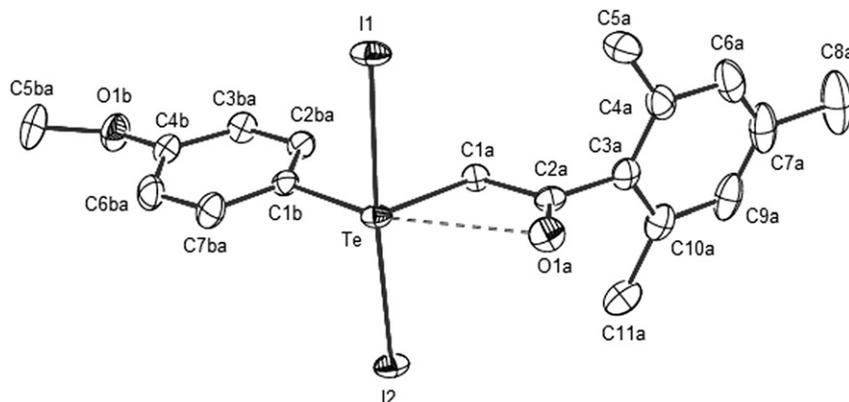


Fig. 5. Molecular structure of **4c**. Selected interatomic distances (Å) and angles ($^{\circ}$): Te–C(1a) = 2.144(3), Te–C(1b) = 2.126(4), Te–I(1) = 2.9187(3), Te–I(2) = 2.8831(3), Te \cdots O = 2.903(3); C(1a)–Te–C(1b) = 98.6(1), I(1)–Te–I(2) = 175.29(1), O1a \cdots Te–C1b = 151.6(1).

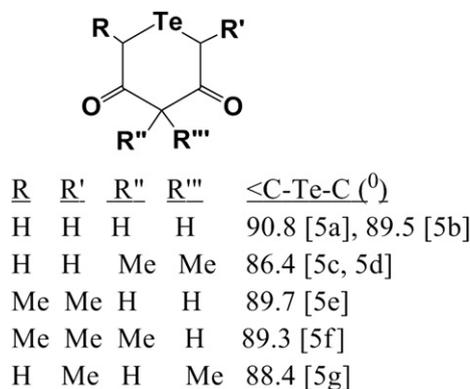


Fig. 6. Crystallographically Characterized Substituted Pentane-2, 4-dionato-C1, C5-tellurium(II) Chelates.

Compound 3: **3a** was reduced in the same way as **2a** to afford yellow needles (from hexane at $-10\text{ }^{\circ}\text{C}$) of the telluride **3**. Yield: 0.19 g (45%). M.p.: $40\text{--}41\text{ }^{\circ}\text{C}$. Anal. Calcd. for $\text{C}_{21}\text{H}_{20}\text{OTe}$: C, 60.63; H, 4.85; Te, 30.67. Found: C, 61.00; H, 4.52; Te, 31.20. $\nu(\text{CO})$: 1680 cm^{-1} . $^1\text{H NMR}$: $\delta = 2.23$ (s, 9H, *p*-Me, *o*-Me), 4.18 (s, 2H, CH_2), 6.72 (s, 2H, aryl), 7.48–8.15 (m, 7H, aryl) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 19.10$ (*p*-Me), 20.15 (*o*-Me), 20.99 (*o*-Me), 32.20 (CH_2), 115.45, 126.74, 127.02, 128.70, 128.92, 129.83, 130.07, 131.91, 132.28, 132.79, 133.37, 133.41, 133.90, 140.57 (C-aryl), 188.29 (CO) ppm. $^{125}\text{Te}\{^1\text{H}\}$ NMR: $\delta = 423$ ppm.

Compound 4: Reduction of **4a** similarly afforded (MesCOCH₂)AnsTe (**4**) as an orange coloured liquid that was characterized by its bromination to (MesCOCH₂)AnsTeBr₂.

3.5. Oxidative addition of halogens to tellurides 1–4

A solution of the appropriate telluride, prepared by the reduction of 1.00 mmol of **1b** (0.61 g) for **1**; **2a** (0.48 g) for **2**; **3a** (0.49 g) for **3**; and **4a** (0.47 g) for **4**; in CH_2Cl_2 ($\sim 20\text{ mL}$), was cooled to $0\text{ }^{\circ}\text{C}$ and treated dropwise with a solution of 1.00 mmol SO_2Cl_2 (0.14 g) for **1a**; Br_2 (0.16 g) for **2b**, **3b** and **4b**; I_2 (0.25 g) for **1c**, **2c**, **3c** and **4c** in the same solvent ($\sim 10\text{ mL}$) under stirring over a period of 30 min. Concentration of the solution followed by addition of

hexane yielded the corresponding dihalides. Recrystallization from CH_2Cl_2 or CHCl_3 gave analytically pure samples.

Compound 1a: Yield: 0.17 g (66%). M.p.: $224\text{--}225\text{ }^{\circ}\text{C}$. Anal. Calcd. for $\text{C}_{22}\text{H}_{26}\text{Cl}_2\text{OTe}$: C, 50.72; H, 5.03; Te, 24.49. Found: C, 51.00; H, 4.95; Te, 25.10. $\nu(\text{CO})$: 1686 cm^{-1} . $^1\text{H NMR}$: $\delta = 2.29$ (s, 9H, *p*-Me and *o*-Me), 5.00 (s, 2H, CH_2), 6.88 (s, 2H, aryl) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 19.41$ (*p*-Me), 21.15 (*o*-Me), 60.67 (CH_2), 128.99, 133.81, 133.98, 140.27 (C-aryl), 201.57 (CO) ppm. $^{125}\text{Te}\{^1\text{H}\}$ NMR: $\delta = 625$ ppm. λ_{max} in CHCl_3/nm ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$): 254 (36940).

Compound 2b: Yield: 0.37 g (65%). M.p.: $162\text{ }^{\circ}\text{C}$. Anal. Calcd. for $\text{C}_{20}\text{H}_{24}\text{OBr}_2\text{Te}$: C, 42.31; H, 4.26; Te, 22.47. Found: C, 42.52; H, 4.10; Te, 23.00. $\nu(\text{CO})$: 1686 cm^{-1} . $^1\text{H NMR}$: $\delta = 2.32$ (s, 9H, *o*-Me and *p*-Me), 2.34–2.36 (m, 3H, *p*-Me), 2.61–2.65 (m, 3H, *o*-Me), 2.80–2.83 (m, 3H, *o*-Me), 5.38, 5.41, 5.46, 5.48, 5.55 (5 signals due to CH_2 ; combined integration equivalent to 2H), 6.91 (s, 2H, aryl), 6.98 (s, 1H, aryl), 7.01 (s, 1H, aryl) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 19.34$, 19.43, 20.98, 21.14, 23.33, 23.45, 24.46, 24.72 (*o*-Me, *p*-Me, CH_2), 128.96, 128.99, 130.37, 130.44, 131.03, 131.47, 131.51, 132.64, 133.81, 133.88, 133.97, 134.30, 134.48, 139.59, 139.78, 140.32, 140.35, 141.16, 141.22, 142.29, 142.31 (C-aryl), 201.66, 201.70 (CO) ppm. $^{125}\text{Te}\{^1\text{H}\}$ NMR: $\delta = 716$, 672 (1:1) ppm.

Compound 3b: Yield: 0.38 g (62%). M.p.: $172\text{ }^{\circ}\text{C}$. Anal. Calcd. for $\text{C}_{21}\text{H}_{20}\text{OBr}_2\text{Te}$: C, 43.80; H, 3.50; Te, 22.16. Found: C, 44.10; H, 3.20; Te, 23.00. $\nu(\text{CO})$: 1688 cm^{-1} . $^1\text{H NMR}$: $\delta = 2.32$ (s, 3H, *p*-Me), 2.40 (s, 6H, *o*-Me), 5.59 (s, 2H, CH_2), 6.92 (s, 2H, aryl), 7.53–8.11 (m, 7H, aryl) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 19.45$ (*p*-Me), 21.17 (*o*-Me), 69.30 (CH_2), 126.61, 126.78, 127.46, 128.30, 128.97, 129.04, 129.47, 131.84, 132.68, 133.38, 133.76, 133.97, 134.33, 140.40 (C-aryl), 201.51 (CO) ppm. $^{125}\text{Te}\{^1\text{H}\}$ NMR: $\delta = 671$ ppm.

Compound 4b: Yield: 0.35 g (62%). M.p.: $188\text{ }^{\circ}\text{C}$. Anal. Calcd. for $\text{C}_{18}\text{H}_{20}\text{O}_2\text{Br}_2\text{Te}$: C, 38.90; H, 3.63; Te, 22.96. Found: C, 39.00; H, 3.50; Te, 23.3. $\nu(\text{CO})$: 1684 cm^{-1} . $^1\text{H NMR}$: $\delta = 2.30$ (s, 3H, *p*-Me), 2.35 (s, 6H, *o*-Me), 3.85 (s, 3H, OMe), 5.32 (s, 2H, CH_2), 6.88 (s, 2H, aryl), 6.98 (d, 2H, aryl), 8.07 (d, 2H, aryl) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 19.14$ (*p*-Me), 21.14 (*o*-Me), 55.55 (*o*-Me), 68.93 (CH_2), 114.21, 115.89, 128.99, 133.73, 133.96, 136.71, 140.26, 162.21 (C-aryl), 201.45 (CO) ppm. $^{125}\text{Te}\{^1\text{H}\}$ NMR: $\delta = 769$ ppm.

Compound 1c: Yield: 0.28 g (80%). M.p.: $211\text{ }^{\circ}\text{C}$. Anal. Calcd. for $\text{C}_{22}\text{H}_{26}\text{I}_2\text{OTe}$: C, 37.54; H, 3.72; Te, 18.13. Found: C, 37.15; H, 3.50; Te, 19.00. $\nu(\text{CO})$: 1689 cm^{-1} . $^1\text{H NMR}$: $\delta = 2.29$ (s, 3H, *p*-Me), 2.35 (s, 6H, *o*-Me), 5.17 (s, 2H, CH_2), 6.87 (s, 2H, aryl) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 19.86$ (*p*-Me), 21.15 (*o*-Me), 56.57 (CH_2), 129.08, 133.65, 134.07, 140.35 (C-aryl), 201.85 (CO) ppm. $^{125}\text{Te}\{^1\text{H}\}$ NMR: $\delta = 526$ ppm. λ_{max} in CHCl_3/nm ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$): 282 (20050), 346 (7780).

Compound 2c: Yield: 0.46 g (69%). M.p.: $125\text{ }^{\circ}\text{C}$. Anal. Calcd. for $\text{C}_{20}\text{H}_{24}\text{OI}_2\text{Te}$: C, 36.30; H, 3.66; Te, 19.28. Found: C, 36.50; H, 3.55; Te, 19.50. $\nu(\text{CO})$: 1685 cm^{-1} . $^1\text{H NMR}$: $\delta = 2.262.77$ (m, 18H, 6 Me), 4.23, 5.60 (two signals assignable to CH_2 in the ratio 36:64; combined integration equivalent to 2H), 6.87–7.03 (m, 4H, aryl) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 19.98$, 21.00, 21.17, 23.14, 25.73 (*o*-Me, *p*-Me), 30.79 (CH_2), 126.15, 127.21, 128.67, 129.13, 130.68, 131.63, 133.62, 133.93, 134.27, 138.86, 140.48, 141.51, 142.02, 147.15 (C-aryl), 201.88 (CO) ppm. $^{125}\text{Te}\{^1\text{H}\}$ NMR: $\delta = 550$ ppm.

Compound 3c: Yield: 0.41 g (60%). M.p.: $147\text{ }^{\circ}\text{C}$. Anal. Calcd. for $\text{C}_{21}\text{H}_{20}\text{OI}_2\text{Te}$: C, 37.66; H, 3.01; Te, 19.05. Found: C, 37.80; H, 3.00; Te, 19.50. $\nu(\text{CO})$: 1683 cm^{-1} . $^1\text{H NMR}$: $\delta = 2.33$ (s, 3H, *p*-Me), 2.46 (s, 6H, *o*-Me), 5.61 (s, 2H, CH_2), 6.92 (s, 2H, aryl), 7.55–8.10 (m, 7H, aryl) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 20.02$ (*p*-Me), 21.18 (*o*-Me), 65.43 (CH_2), 123.63, 126.90, 127.03, 127.58, 128.20, 129.18, 129.43, 131.82, 132.34, 133.41, 133.70, 134.16, 134.29, 140.53 (C-aryl), 201.67 (CO) ppm. $^{125}\text{Te}\{^1\text{H}\}$ NMR: $\delta = 574$ ppm.

Compound 4c: Yield: 0.39 g (60%). M.p.: $150\text{ }^{\circ}\text{C}$. Anal. Calcd. for $\text{C}_{18}\text{H}_{20}\text{O}_2\text{I}_2\text{Te}$: C, 33.27; H, 3.10; Te, 19.64. Found: C, 33.60; H, 3.00; Te, 20.10. $\nu(\text{CO})$: 1682 cm^{-1} . $^1\text{H NMR}$: $\delta = 2.31$ (s, 3H, *p*-Me), 2.41 (s, 6H, *o*-Me), 3.85 (s, 3H, *o*-Me), 5.39 (s, 2H, CH_2), 6.88 (s, 2H, aryl),

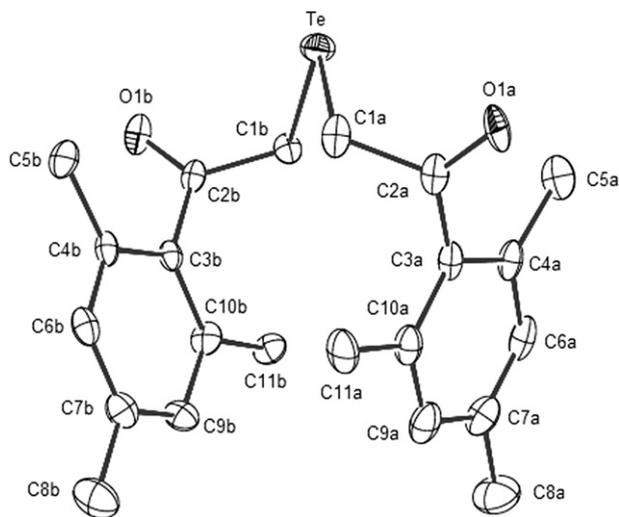


Fig. 7. Molecular structure of **1**. Selected interatomic distances (\AA) and angles ($^{\circ}$): Te–C1a = 2.148(4), Te–C1b = 2.153(4), Te...O1a = 3.603(3), Te...O1b = 3.586(2); C1a–Te–C1b = 97.3(2), O1a...Te–C1b = 109.69(9), O1b...Te–C1a = 106.4(1).

6.90 (d, 2H, aryl), 7.99 (d, 2H, aryl) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR: δ = 20.02 (p-Me), 21.16 (o-Me), 55.53 (o-Me), 65.69 (CH₂), 109.06, 116.25, 129.15, 133.34, 134.31, 138.21, 140.40, 161.96 (C-aryl), 201.64 (CO) ppm. $^{125}\text{Te}\{^1\text{H}\}$ NMR: δ = 685 ppm.

3.6. Metathetical reactions of **1b**, **2a**, **3a** and **4a**

Compound **1c** was obtained in a better yield when **1b** (0.61 g, 1.00 mmol) and KI (0.33 g, 2.00 mmol) were stirred together in dichloromethane (15 mL) for ~3 h. Potassium halides were removed by filtration. Addition of petroleum ether and cooling afforded yellow crystals of **1c**. Yield: 0.60 g (85%).

Compounds **2c** (yield: 80%), **3c** (yield: 69%) and **4c** (yield: 94%) were prepared in a similar way.

3.7. Alternative procedures for synthesis of **2b**, **3b** and **1a**

Compounds 2b and 3b: To a suspension of MesTeBr (prepared in situ from Mes₂Te₂ (0.25 g, 0.50 mmol) and Br₂ (0.08 g, 0.50 mmol) in chloroform at 0 °C) was added a solution of α -bromo-2,4,6-trimethylacetophenone (0.32 g, 2.00 mmol) in the same solvent at room temperature. The reaction mixture was stirred for 12 h and then passed through a short silica column. Addition of petroleum ether (40–60 °C) to the concentrated solution and cooling afforded **2b** as a light yellow solid. Yield: 0.14 g (30%). M.p.: 160–162 °C.

Under similar conditions Np₂Te₂ (0.25 g, 0.50 mmol) afforded **3b**. Yield: 0.13 g (28%). M.p.: 172 °C.

Compound 1a: A solution of TeCl₄ (0.68 g, 2.5 mmol) and 2,4,6-trimethylacetophenone (1.60 g, 5.0 mmol) in dry chloroform (15 mL) was heated to reflux for 3 h, cooled and filtered through a short silica column. Concentration of the resulting solution and addition of petroleum ether afforded colourless crystalline solid, (MesCOCH₂)₂TeCl₂, **1a**. Yield: 0.41 g (78%). M.p. 225 °C.

3.8. Reaction of **1b–3b** with ketones

Compound **1b** (1.0 mmol) was stirred with 5 mL of acetone, acetophenone or pinacolone at room temperature for 3 h. Removal of volatiles under reduced pressure afforded unreacted **1b**. Likewise, **2b** and **3b** were recovered unchanged from the reaction mixture.

3.9. Crystallography

Single crystals suitable for X-ray crystallography were grown by slow evaporation of dichloromethane solutions of **1b**, **3a** and **4c**; ether solutions of **2a**, **2b** and **2c** and cooling of concentrated hexane solutions of **1**, **2** and **3** to –10 °C. Intensity data were collected on an Oxford Diffraction Gemini CCD diffractometer with graphite-monochromated Mo-K α (0.7107 Å) radiation. Data were reduced and corrected for absorption using the programs SAINT and SADABS [14]. The structures were solved by direct methods and difference Fourier synthesis using SHELXS-97 and ORTEP figures generated using the program WinGX 2002 [15]. Full-matrix least-squares refinements on F^2 , using all data, were carried out with anisotropic displacement parameters applied to non-hydrogen atoms. The anisyl group of **4c** is two-fold disordered with occupancies of 0.554 (8):0.45. Hydrogen atoms attached to carbon were included in

geometrically calculated positions using a riding model and were refined isotropically.

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Appendix A. Supplementary material

CCDCs 770267, 770268, 770269, 770270, 770271, 770272, 770273, 770274 and 770275 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found in the online version, at doi: 10.1016/j.jorganchem.2010.05.022.

References

- [1] D. Seyferth, *Organometallics* 20 (2001) 2940–2955.
- [2] K.J. Irgolic, *The Organic Chemistry of Tellurium*. Gordon and Breach, New York, 1974.
- [3] (a) A.K.S. Chauhan, A. Kumar, R.C. Srivastava, R.J. Butcher, *J. Organomet. Chem.* 658 (2002) 169–175; (b) A.K.S. Chauhan, A. Kumar, R.C. Srivastava, J. Beckmann, A. Duthie, R. J. Butcher, *J. Organomet. Chem.* 689 (2004) 345–351.
- [4] I.D. Sadekov, V.Z. Alexander, A.M. Alexander, *Sulfur Rep.* 23 (2002) 125–207.
- [5] (a) J.C. Dewan, J. Silver, *Acta Crystallogr. B* 33 (1977) 1469–1473; (b) C.L. Raston, R.J. Secomb, A.H. White, *J. Chem. Soc., Dalton* (1976) 2307–2310; (c) J.C. Dewan, J. Silver, *Inorg. Nucl. Chem. Lett.* 12 (1976) 647–649; (d) J.C. Dewan, J. Silver, *J. Chem. Soc., Dalton* (1977) 644–647; (e) J.C. Dewan, J. Silver, *Aust. J. Chem.* 30 (1977) 487–493; (f) J.C. Dewan, J. Silver, *Acta Crystallogr. B* 33 (1977) 2671–2674; (g) J.C. Dewan, J. Silver, *J. Organomet. Chem.* 125 (1977) 125–139; (h) M.R. Smith, M.M. Mangion, R.A. Zingaro, E.A. Meyers, *J. Heterocycl. Chem.* 10 (1973) 527–531.
- [6] A.K.S. Chauhan, Anamika, A. Kumar, R.C. Srivastava, R.J. Butcher, *J. Organomet. Chem.* 690 (2005) 313–321.
- [7] (a) E. Hevia, K.W. Henderson, A.R. Kennedy, R.E. Mulvey, *Organometallics* 25 (2006) 1778–1785; (b) S.E. Baillie, E. Hevia, A.R. Kennedy, R.E. Mulvey, *Organometallics* 26 (2007) 204–209; (c) D.R. Armstrong, A.M. Drummond, L. Balloch, D.V. Graham, E. Hevia, A. R. Kennedy, *Organometallics* 27 (2008) 5860–5866 and references therein.
- [8] A.K.S. Chauhan, P. Singh, A. Kumar, R.C. Srivastava, R.J. Butcher, A. Duthie, *Organometallics* 26 (2007) 1955–1959.
- [9] J. Beckmann, M. Hesse, H. Poleschner, K. Sappelt, *Angew. Chem., Int. Ed.* 46 (2007) 8277–8280 and references therein.
- [10] (a) T. Hama, X. Liu, D.A. Culkin, J.F. Hartwig, *J. Am. Chem. Soc.* 125 (2003) 11176–11177; (b) T. Hama, X. Liu, D.A. Culkin, J.F. Hartwig, *J. Am. Chem. Soc.* 128 (2006) 4976–4985; (c) P. Powell, *Principles of Organometallic Compounds*, second ed. Chapman and Hall, London, New York, 1988, p. 59 (Chapter 3); (d) An X-ray study on BrZnCH₂CO₂Et however suggests simultaneous formation of a Zn–C and a Zn–O bond in the dimer J. Dekker, P.H.M. Budzelaar, J. Boersma, G.J.M. van der Kerk, *Organometallics* 3 (1984) 1403–1407.
- [11] F.H. Allen, O. Kannard, *Chem. Des. Automat. News* 8 (1993) 1.
- [12] L. Engman, *Organometallics* 6 (1986) 427–431.
- [13] C.O. Guss, *J. Am. Chem. Soc.* 75 (1953) 3177–3179.
- [14] SMART, SAINT and SADABS. Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA, 1999.
- [15] (a) L.J. Farrugia, *J. Appl. Crystallogr.* 32 (1999) 837–838; (b) L.J. Farrugia, *J. Appl. Crystallogr.* 30 (1997) 565.